



# **Modular Process Equipment for Low Cost Manufacturing of High Capacity Prismatic Li-Ion Cell Alloy Anodes**

**2013 DOE Vehicle Technologies Program Annual Merit Review**

**Project ID#: ES128**

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**Project Manager: Ajey M. Joshi**

**Energy & Environmental Solutions**

**Alternative Energy Products**

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# Overview

## Timeline

Project Start	Oct. 1, 2011
Project End	Sep. 30, 2014
Percent Complete	~33%

## Barriers Addressed

- *Cost of manufacturing*
- *Cycling lifetime of high capacity materials*
- *Prismatic cell format*

## Budget

### Total Project Funding

DOE Share: 51% (\$4.90M)

Applied Materials: 49% (\$4.63M)

FY12 Funding Received: \$1.6M

FY13 Funding Expected\*: \$1.7M

\*DOE Share

## Partners

- J. Nanda, Oak Ridge National Laboratory
- G. Liu, Lawrence Berkeley National Laboratory
- M. Yakovleva, FMC Lithium
- V. Vu, A123 Navitas Systems
- K. Adjemian, Nissan-TCNA

# Summary of the Project Objectives

## Low Cost Manufacturing of High Capacity Prismatic Li-Ion Cell Alloy Anodes

### ▪ A. PROJECT OBJECTIVES

The objective of this project is to research, develop, and demonstrate novel high capacity Li-ion battery cell anodes that are capable of achieving an energy density of at least 500 Watthours per liter (Wh/l) and a power density of at least 500 Watts per liter (W/l) while maintaining comparable performance standards in terms of cycle life (300-1000 cycles at 80% depth of discharge), calendar life (5-10 years), and durable cell construction and design capable of being affordably mass produced.

### ▪ B. PROJECT SCOPE

The project includes research, development, test, and demonstration of an advanced High Volume Manufacturing (HVM) prototype module for fabricating high capacity Li-ion anodes in a continuous roll-to-roll configuration at low cost. The HVM prototype module will manufacture a new class of Li battery anodes with a high capacity based on an innovative micro-cell porous 3D Cu – Li alloy structure. The project will focus on demonstrating the innovative high rate deposition technique suitable for the micro-cell porous 3D Cu – Li alloy architecture.

# Technical Summary

## Baseline Characterization:

- A cell level design model has been developed for two chemistry combinations,
  - baseline cell having  $\text{Li}_{1-x}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$  (NMC333) positive electrode with 3D Cu Graphite negative electrode, and
  - interim cell having NMC positive electrode with 3D CuSn negative electrode.

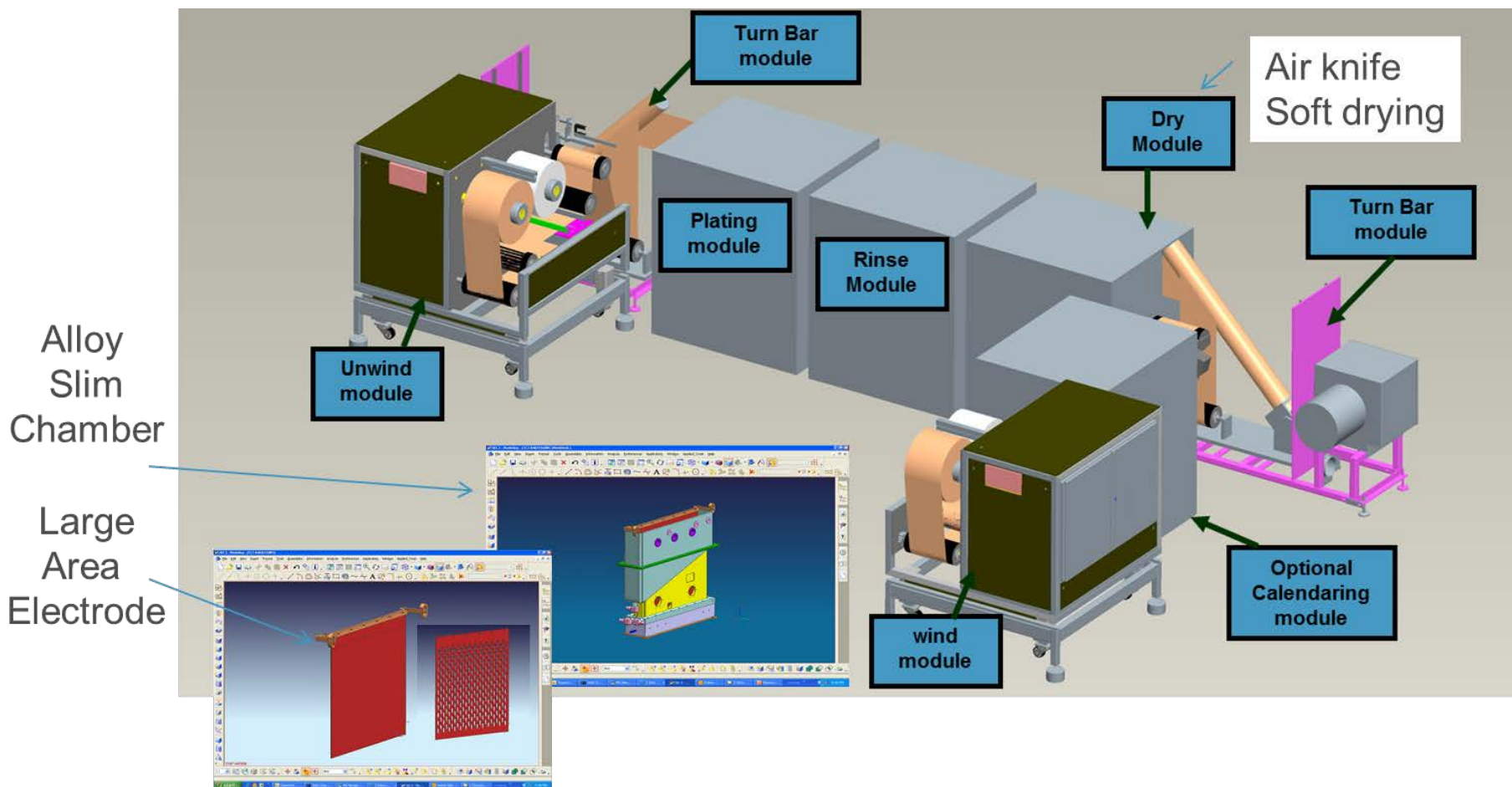
## Technology Design:

- Experimental development focused on concept design of initial electro-deposition module which allows for 3D porous structure formation in a single prototype tool for both 3D Cu collector and 3D CuSnFe alloy anode coating.
  - Baseline processes have been developed for (a) 3D Cu current collector and (b) for Graphite coating using a water soluble process.
  - Scanning Electron Microscopy (SEM) analysis of 3D Cu Graphite structures shows pore fill and crack-free coating. Preliminary testing rate performance in half-cell assembly vs. Li demonstrated capacity retention advantages at 2C and 3C.

## Technology Development:

- For the high capacity, we have developed CuSnFe electro-deposition process and obtained nano-structure alloy for high loading NMC / CuSnFe cell testing.

# Schematic Design of the Modular Equipment for 3D-structure Formation on Cu Foil



# 3D Cu Anode Development Roadmap

Goal: to Develop Next Generation 3D Anode

Capacity  
Current loading  
Cycling lifetime

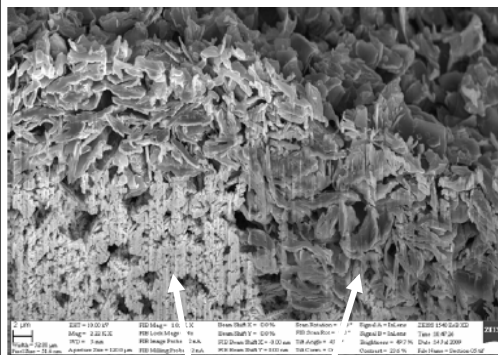
1000

750

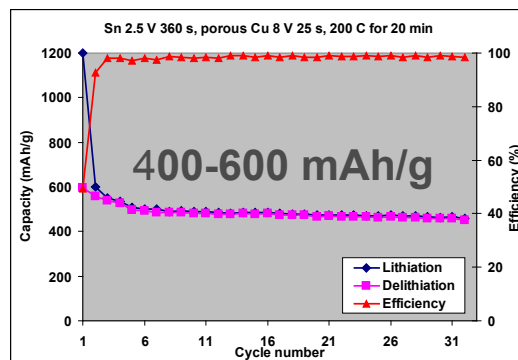
500

250

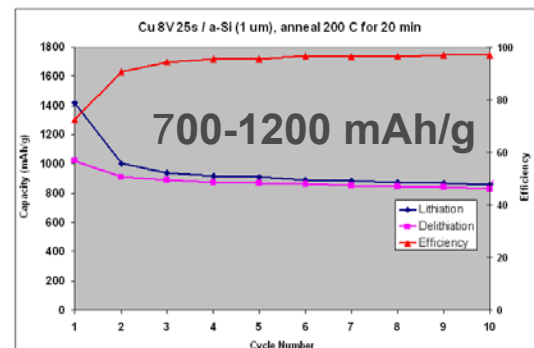
Capacity, mAh/g



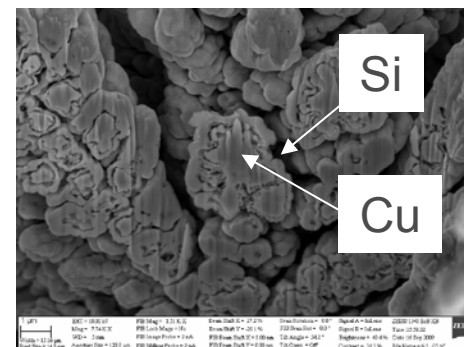
3D Cu + Graphite



3D CuSnFe



3D CuSnFe + Si



3D electrode concept

← Current Technology

Reduced Anode Cost (\$/m<sup>2</sup>) and (\$/Wh) at Higher Performance

Collaboration: A123 Navitas (cell development), FMC (pre-lithiation), LBNL (conductive binder), Nissan-TCNA (testing), ORNL (characterization)

# Technical Summary:

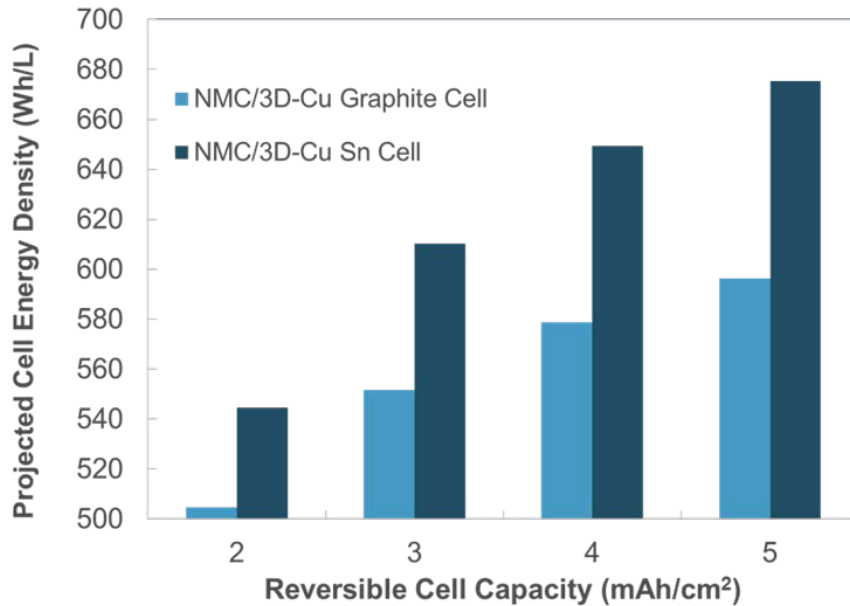
## Prismatic Li-ion Cell Assembly and Test

### Cell Accomplishments

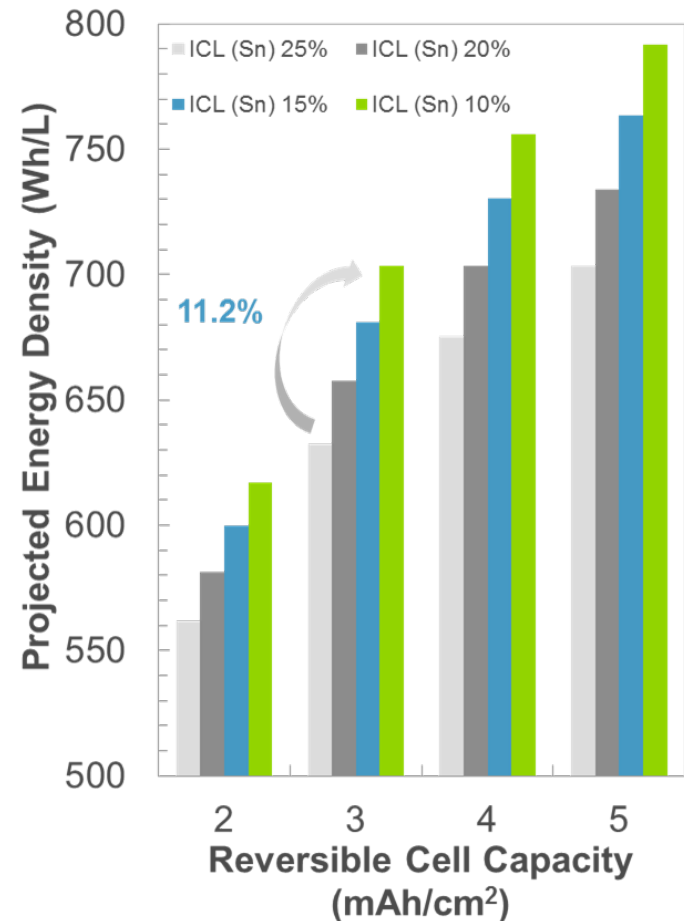
- Assembling and testing full prismatic cells with 3D current collectors resulted in Coulombic efficiency of 99.96% at cycles 160-850.
- The projected lifetime was estimated at ~1300 cycles for 3DCu/Graphite anode baseline cells.
- The projected lifetime was estimated at ~800 cycles for 3DCuSnFe/Graphite anode interim cells at 80% capacity retention at C/3 rate.
- Modular process steps were developed for forming 3-3.5 mAh/cm<sup>2</sup> cells including process methodology for Graphite coating by water soluble process to achieve adhesion to the 3D porous structures. Testing rate performance in half-cell assembly vs. Li demonstrated capacity retention advantages up to 25-27% at 2C and 3C-rates.

# Modeling Results:

## Cell Level Design for Baseline and Interim Cells



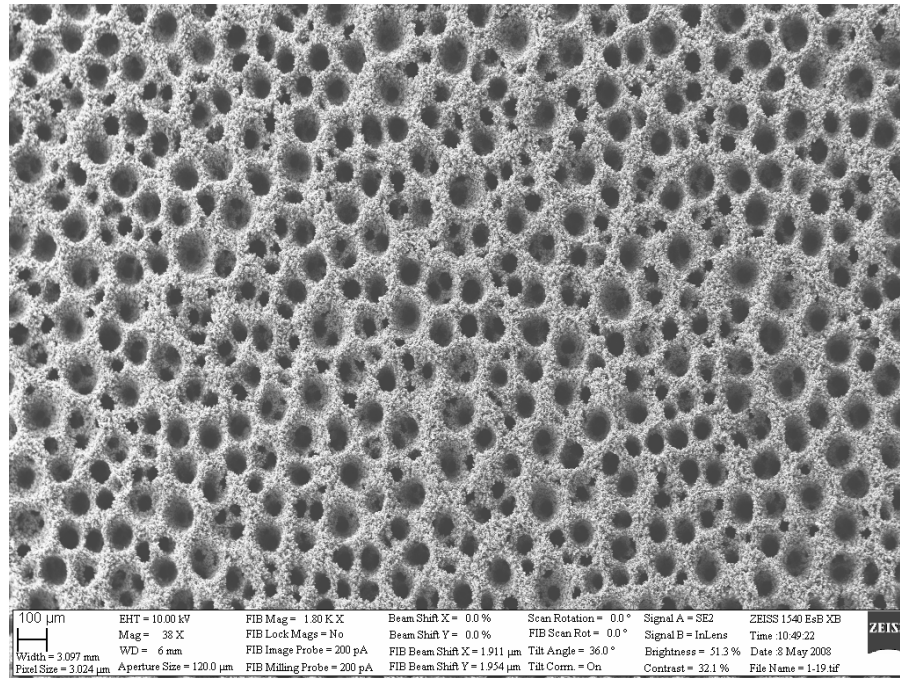
**Project Target >500 Wh/L**



**Energy Density of up to 750 Wh/L is achievable by reducing Irreversible Capacity Loss (ICL)**

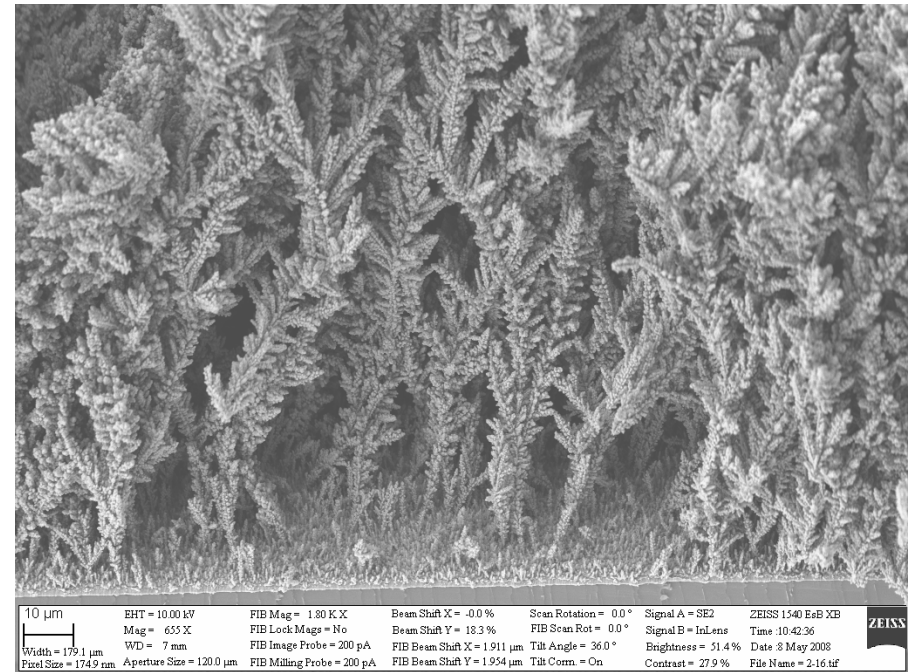
# 3D Cu Plated on Cu Foil: Structural Analysis

## Top View



100  $\mu\text{m}$

## Cross-Sectional View



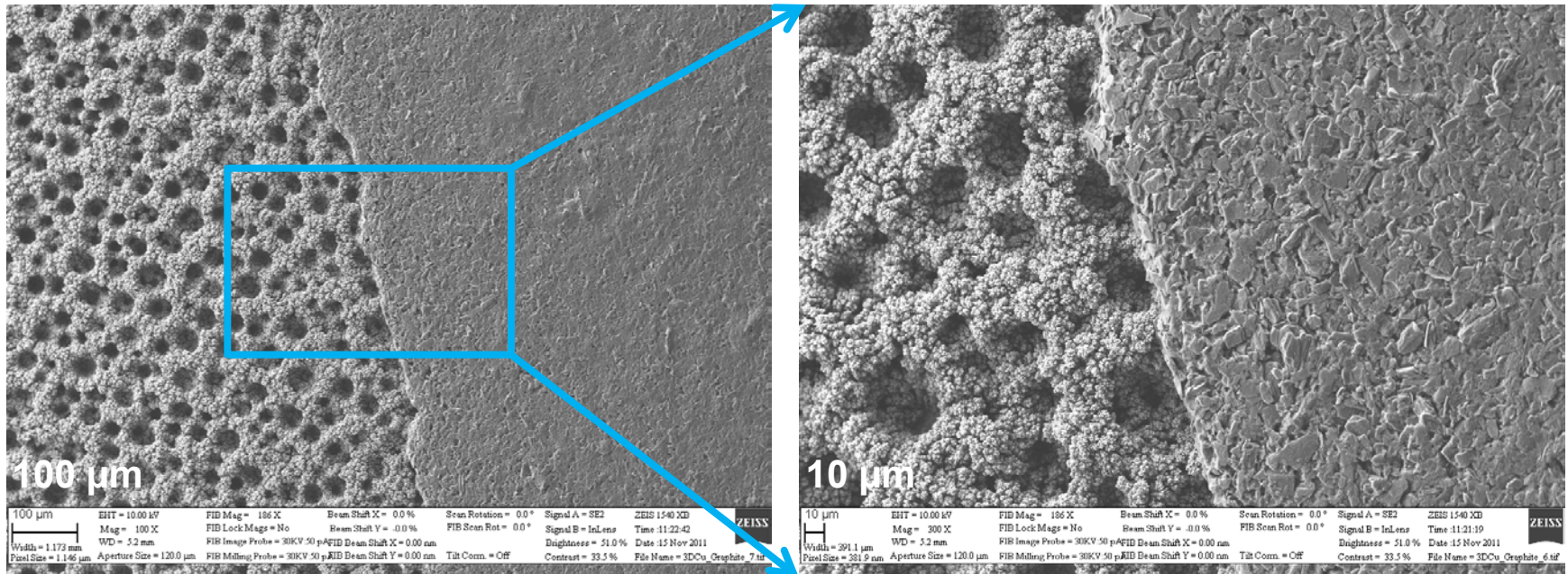
10  $\mu\text{m}$

## 3D Cu Porous Structure Showing Micro, Meso and Nano Porosity

# Water Based Process for Graphite Coating on 3D Cu

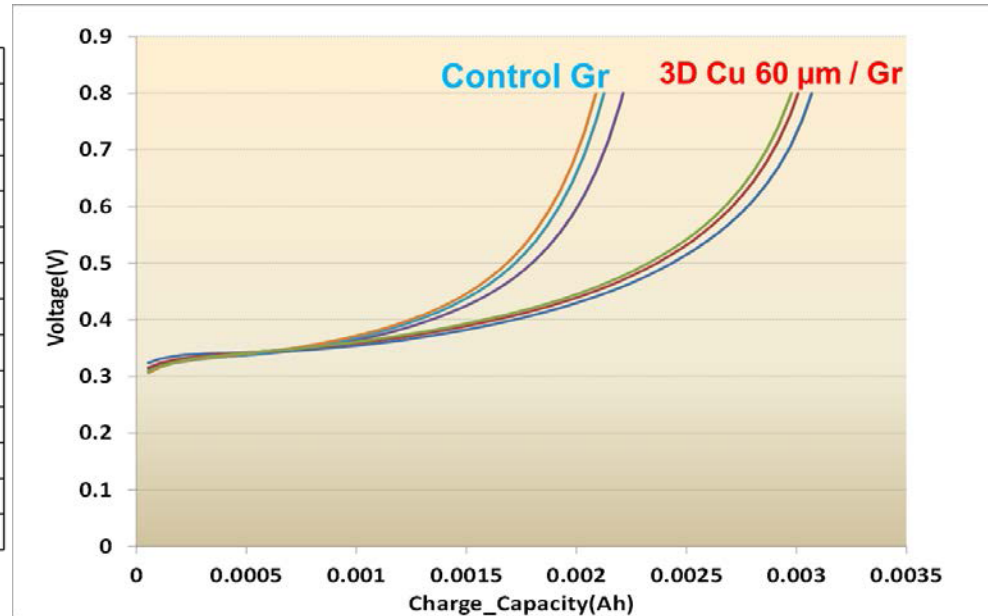
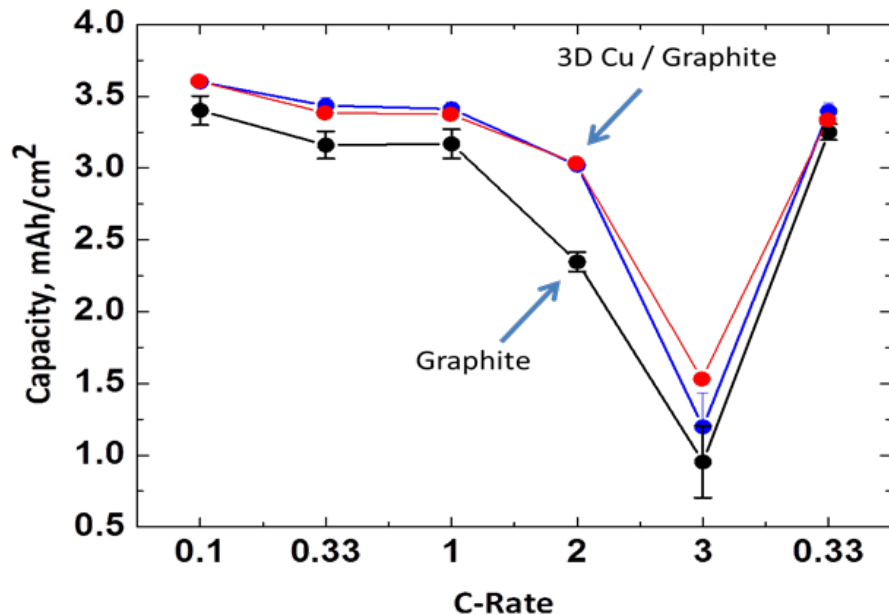
SEM lower magnification  
3D Cu                      Graphite

SEM higher magnification  
3D Cu                      Graphite



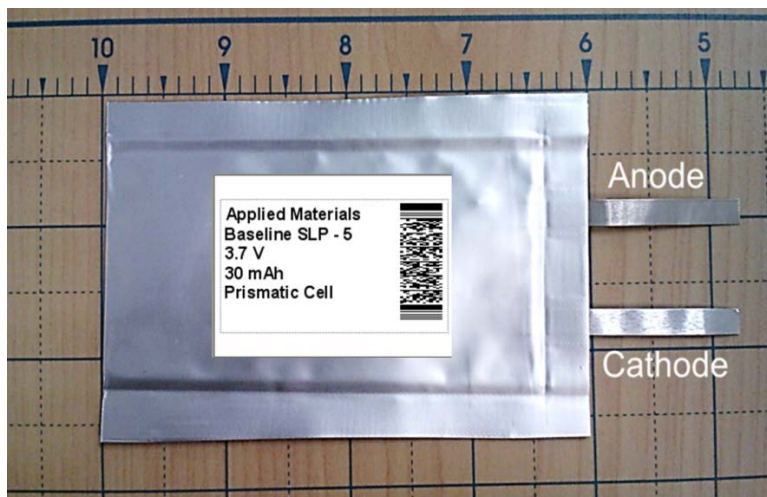
**Thick Graphite Coating with Good Adhesion and No Cracking**

# C-Rate Advantages of 3D Cu / Graphite in Half Cell Tests at $>3$ mAh/cm<sup>2</sup> Loadings



- Charge Capacity of Control Graphite and 3D Cu 60  $\mu$ m / Graphite Samples at different C-rates
- Charge Capacity of Control Graphite and 3D Cu 60  $\mu$ m / Graphite Samples at 2C rate (Half Cell)

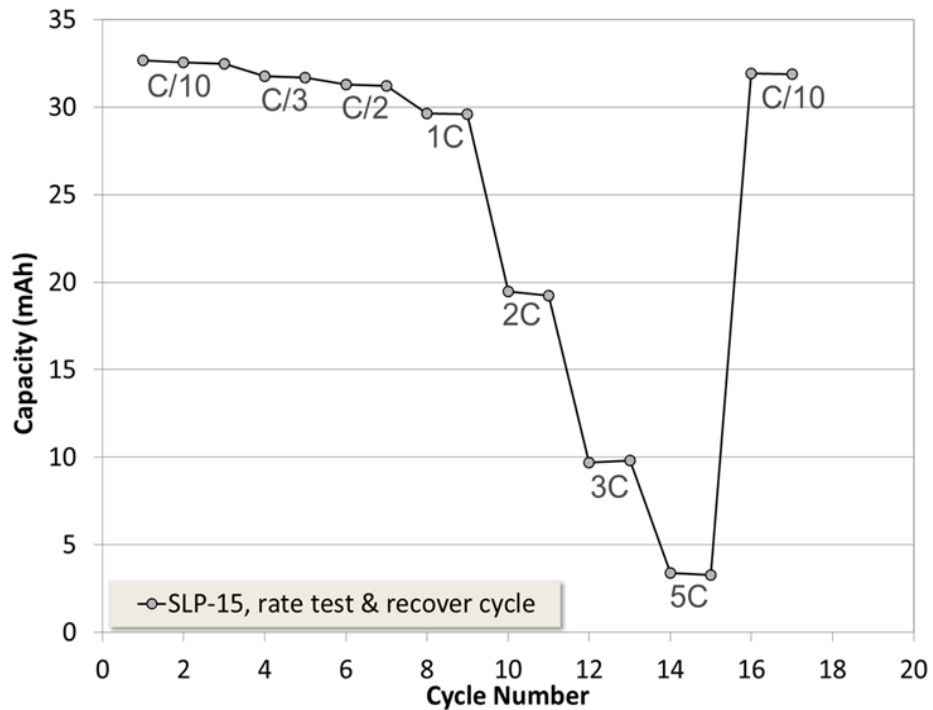
# Full Cells Assembled at Applied and ORNL



# Baseline Cells Characterization Results

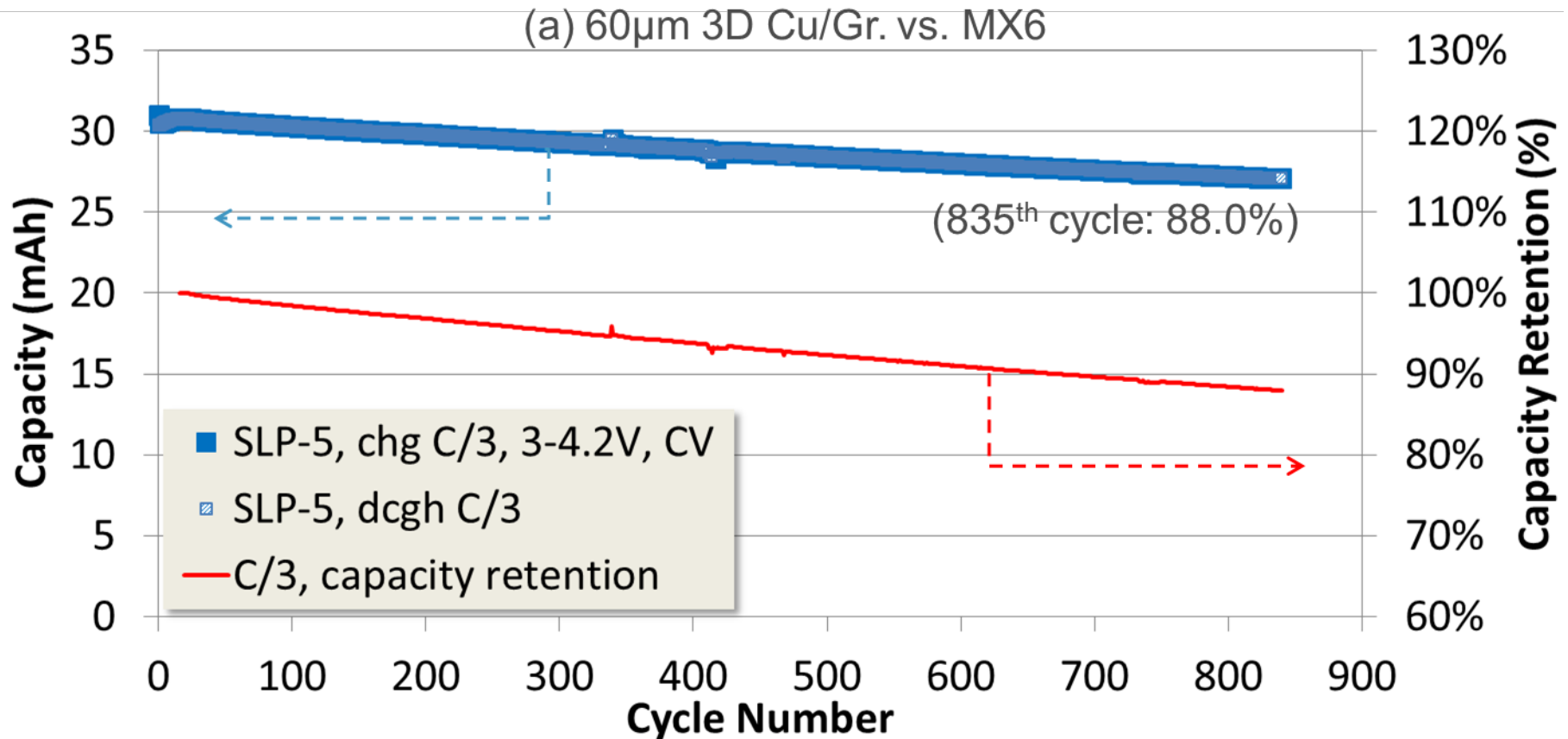
SLP #	Cathode (Code/Weight (mg))	Anode (Code/Weight (mg))	1st Cycle Loss	Cell Capacity after Formation
6	D0426/253.2	E0717-2/196.4	21%	33mAh
7	D0426/268.8	E0717-3/200.9	21%	34mAh
13	W0820/273.4	E1003-2/218.5	20%	37mAh
14	W0820/269.8	E1003-3/211.0	20%	37mAh
15	T90925/245.4	E1005-4/181.7	26%	32mAh
16	T90925/245.3	E1005-4/183.0	33%*	32mAh
17	T90925/239.5	E1008-2/189.1	26%	30mAh
18	T90925/239.5	E1008-2/187.4	23%	30mAh
19	T90925/243.8	E1012-2/193.3	23%	31mAh
20	T90925/242.8	E1012-2/192.7	21%	32mAh

\*Electrolyte leakage occurred during the 1<sup>st</sup> cycle, while cell capacity restored after cell re-sealing.



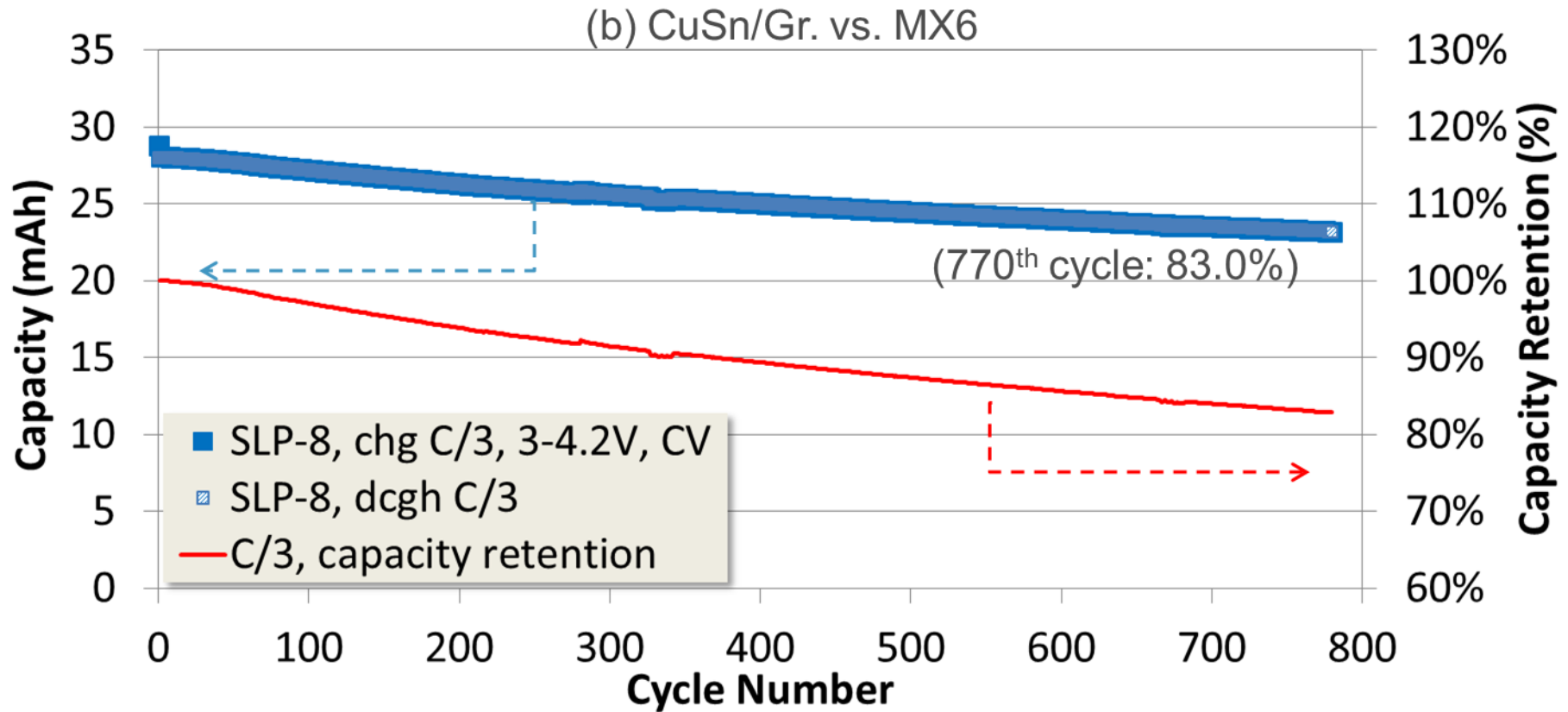
- **Baseline cells for Project Year 2 deliverables. All listed SLP cells are consisted with 60 $\mu$ m 3DCu/Graphite as anode and NMC (MX6, Umicore) as cathode.**

# Baseline Cell Cycling Test Results



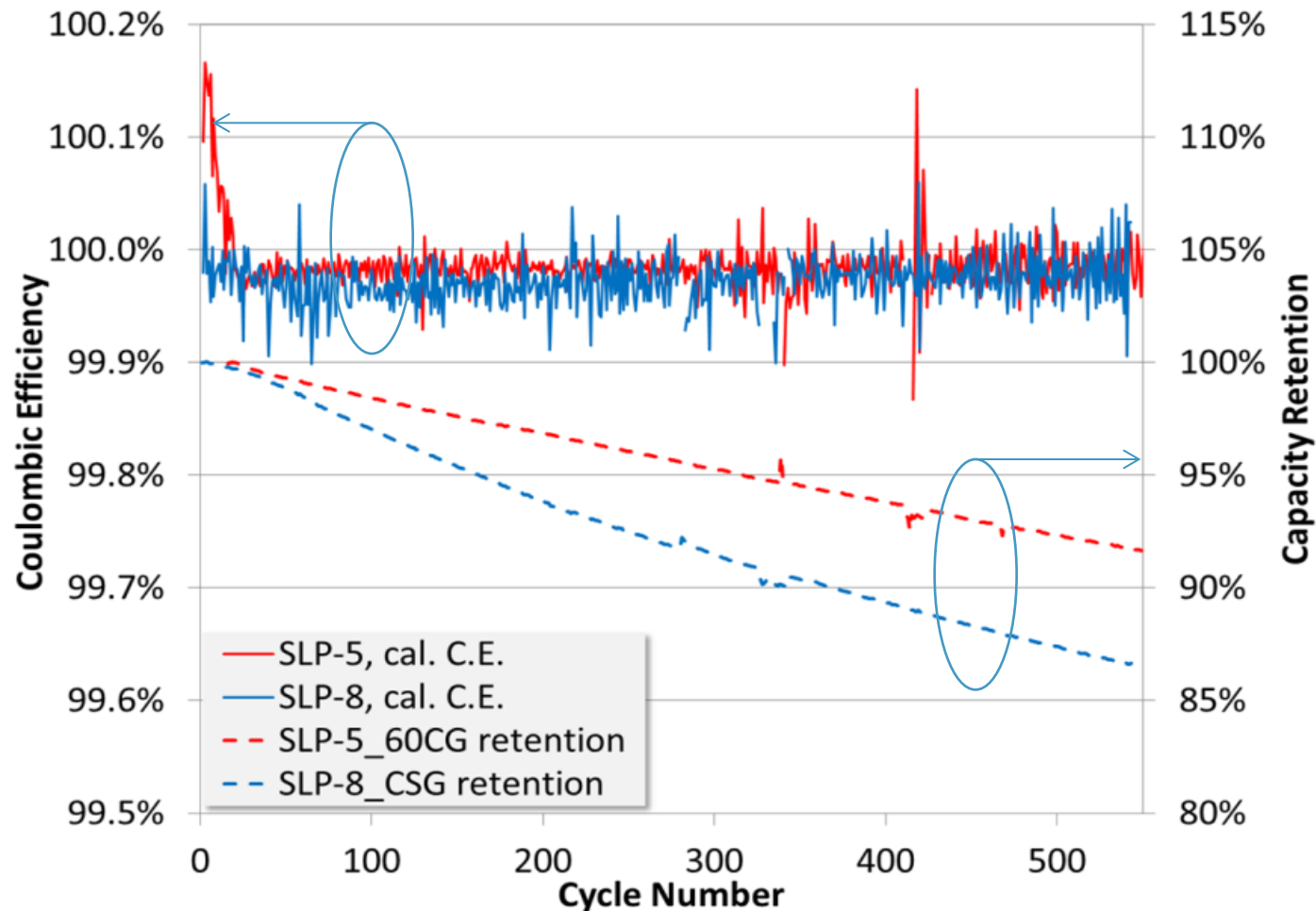
- Single layer pouch cell SLP-5 with 60 $\mu$ m 3D Cu/Graphite anode and NMC cathode

# Interim Cell Cycling Test Results



- Single layer pouch cell SLP-8 with 3D CuSnFe/Graphite anode and NMC cathode

# Coulombic Efficiency and Capacity Retention



- **Red line:** single layer pouch cell SLP-5 with 60µm 3D Cu/Graphite anode and NMC cathode

- **Blue line:** single layer pouch cell SLP-8 with 3D CuSnFe/Graphite anode and NMC cathode

# Collaborators

	Partners for Evaluation and Technology Validation
1. Federal Laboratory	Lawrence Berkeley National Laboratory / Dr. G. Liu - Matching anode-cathode for cell balancing, conductive binder and electrolyte additive evaluation
2. Federal Laboratory	Oak Ridge National Laboratory / Dr. J. Nanda - Materials characterization and degradation analysis using advanced spectroscopic techniques (micro-Raman mapping, X-ray characterization, etc.)
3. Industry	FMC Lithium Division / Dr. M. Yakovleva - Stabilized Lithium metal powders and coating on anode structures for pre-lithiation
4. Industry	A123 Navitas Systems / Dr. V. Vu - Evaluation of Applied Materials electrodes using testing equipment for half coin cell, full coin cell, and full scale 63450 prismatic cell.
5. Industry	Nissan Technical Center N. America / Dr. K. Adjemian - Cell performance measurements and final cell validation to USABC requirements.

# Planned Work for 2013

## **Task 3: Baseline Cell Optimization and Deliverable**

- Demonstrate baseline cell process with 3D Cu/Graphite
- Optimize 3 mAh/cm<sup>2</sup> cell assembly and formation
- Complete capacity retention comparative analysis at 2C and 3C
- Develop thick graphite without cracking for > 3.0 mAh/cm<sup>2</sup> cell
- Complete capacity retention analysis with increased thickness at 2C and 3C

## **Deliverable 1: Submit 18 prismatic cells for DOE independent testing**

## **Task 4: Interim Cell Development**

- Optimize high loading CuSnFe/Graphite electrode
- Complete cycling test in full cell assembly
- During this task the interim cell will be built and sent for characterization and analysis at LBNL and ORNL. Grain size, porosity and other parameters will be characterized for the interim cell deliverable. Applied, A123 Navitas Systems and Nissan TCNA will perform work on extending loading of the anode which will be demonstrated in battery unit.

# Project Summary

- The project is in its 2nd year
- Applied Materials designed modules for fabricating high capacity anodes
  - Developed approach includes
    - Depositing 3D electrodes with micro-cell porous structure
    - Water based processing
- Alloy Anode Development showed advantages of selected materials
  - 3D Electrode structures
    - Modeling Energy Density Requirements
    - 3D Electrode Roadmap
    - 3D Cu / Graphite with better Rate Performance at 2C and 3C
    - 3D Cu(SnFe) with Increased Current Loading
    - 3D Cu(SnFe) / Si Nanometer Grain Size Material
- 2013 work includes High Loading Cell Testing
  - 3.0 - 4.5 mAh/cm<sup>2</sup>
    - Cycling Improvements in collaboration with partners
    - Cost Reduction, Manufacturing Economics

# Acknowledgment

**“This material is based upon work supported by the Department of Energy under Award Number DE-EE0005455.”**

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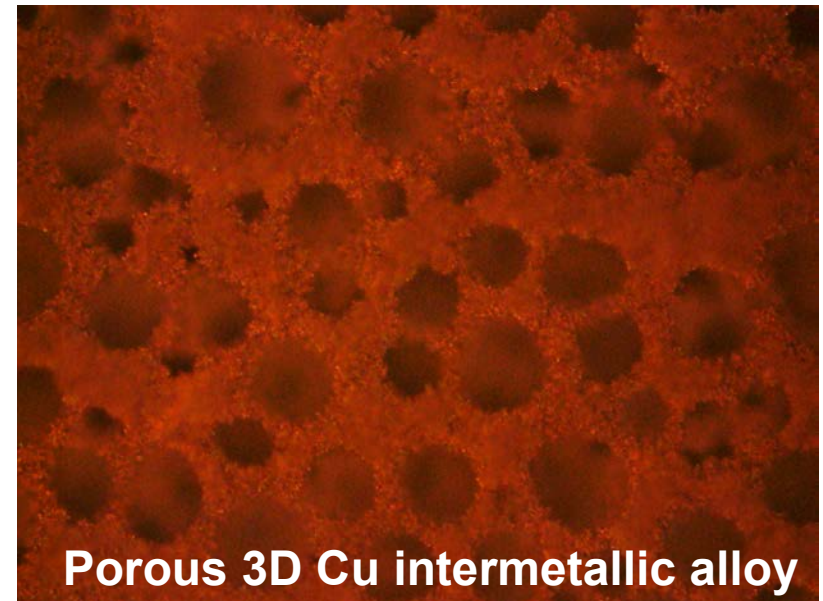
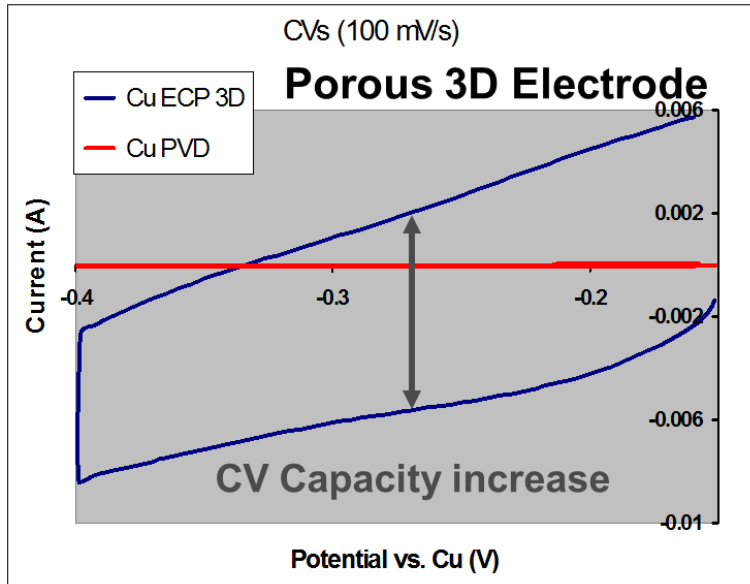
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# Technical Back-Up Slides

# 3D Electrode Concept

- Nano-structured architecture
- Porous Cu plating with dynamic H<sub>2</sub> template



## Advantages of Expanded Area Electrode

- Increased capacity as measured by Cyclic Voltametry (CV)
- Fast charge using high conductivity nanomaterial
- Large energy and power densities

# Plating 3D Cu on Large Surface Area



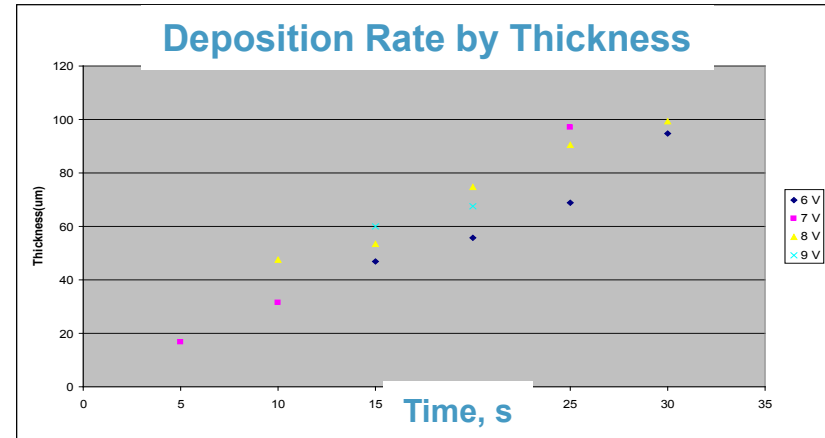
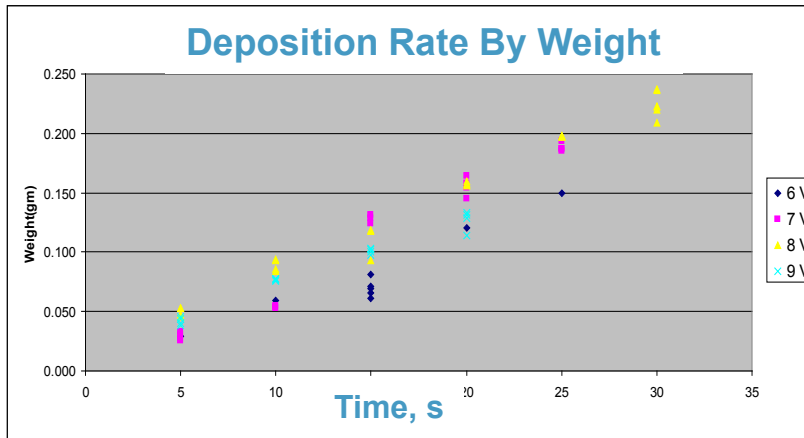
Lab prototype tool



Foil Area 6cm x 30cm



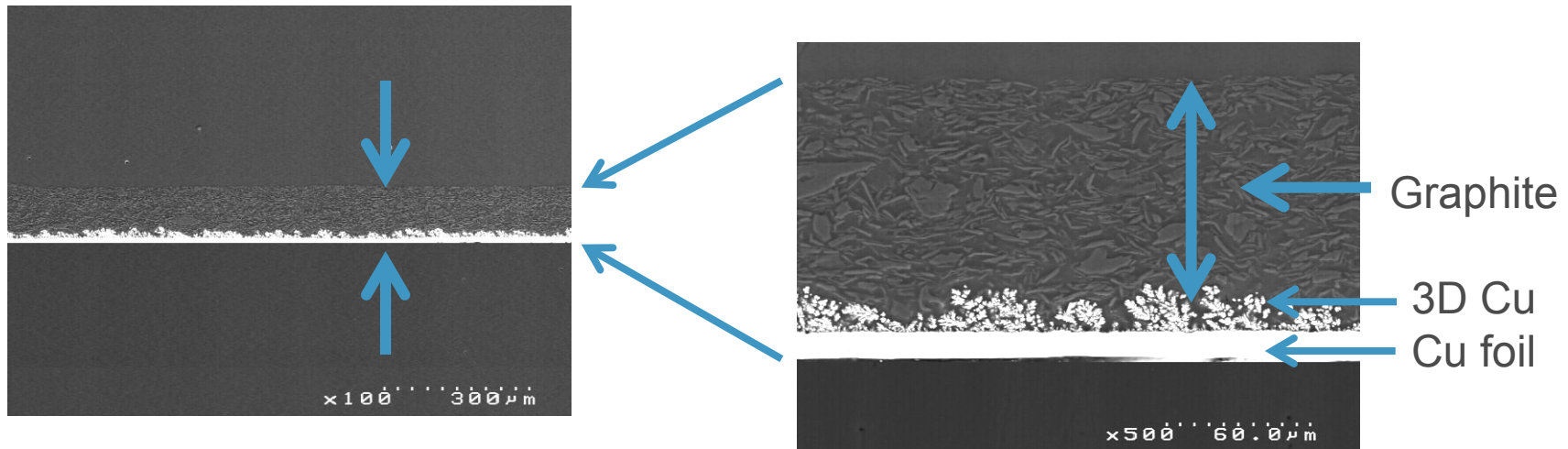
Foil Area 15cm x 20cm



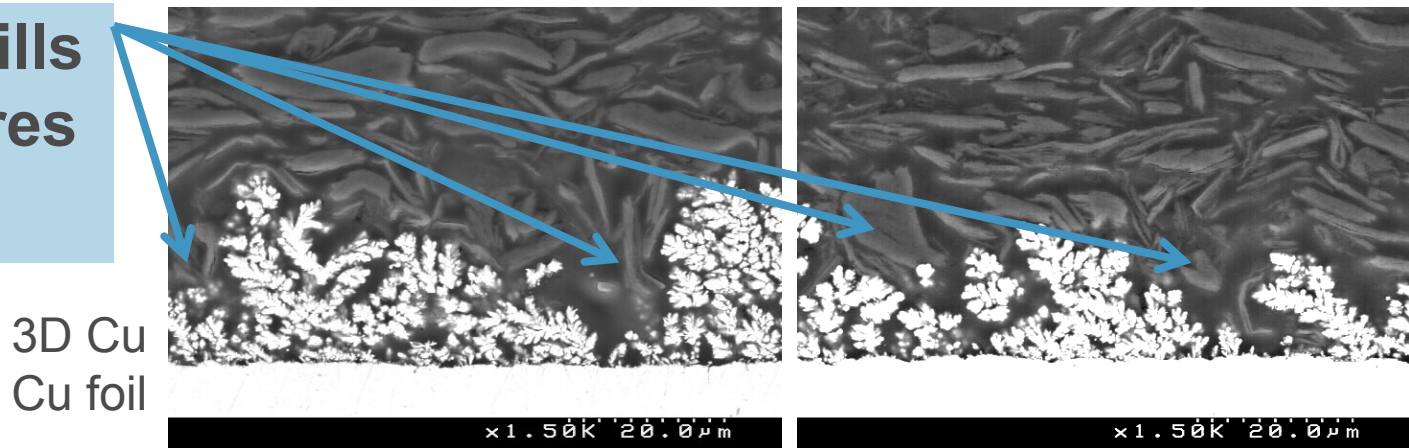
**Deposition Rate Controllable by Both Weight and Thickness**  
**Deposition Rate of 3  $\mu\text{m/s}$  is Many Times Faster than Conventional Approach**

# 150 $\mu\text{m}$ Graphite Fill of 3D Cu Pores without Cracking (SEM cross sections)

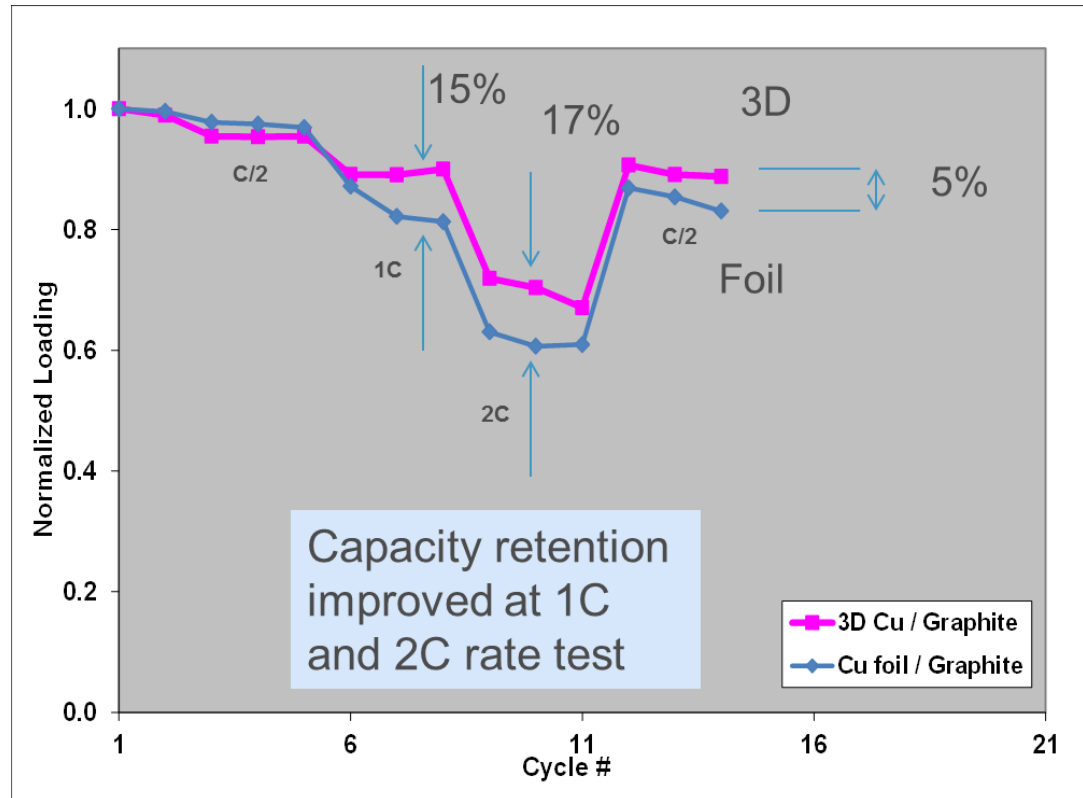
- 150  $\mu\text{m}$  thick graphite



**Graphite fills macro pores in 3D Cu**

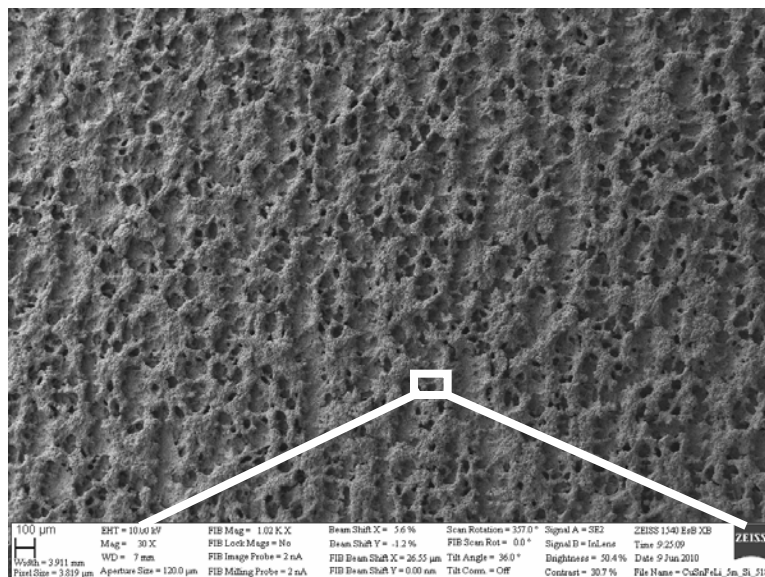


# Capacity Retention Comparison for 3.3 mAh/cm<sup>2</sup> Cells 3D Cu/Graphite vs. Cu Foil /Graphite

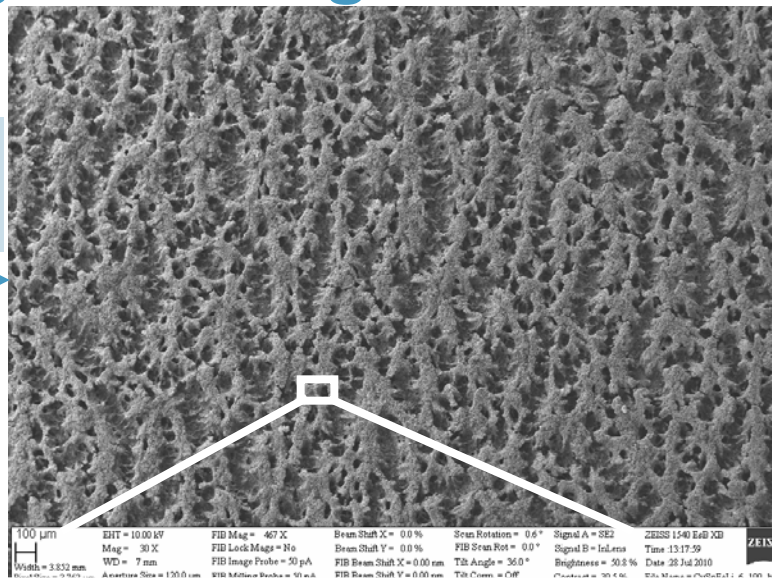


**Up to 17% Capacity Retention Improvement at 2C  
(Baseline Cell)**

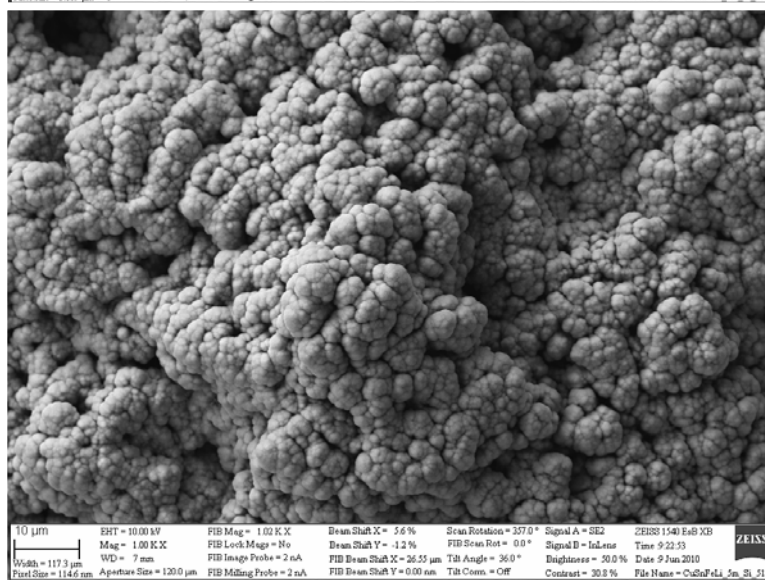
# 3D CuSnFe/Si Anode for High Loading Cell



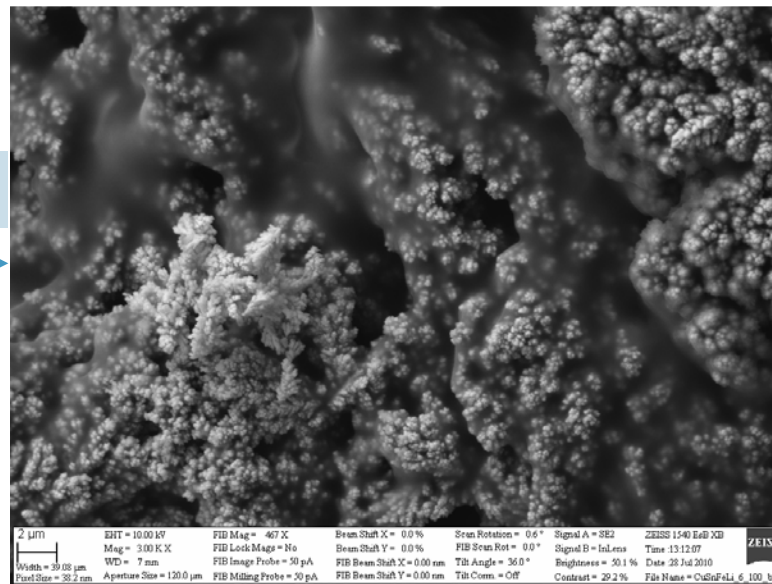
Porosity  
Thickness



Binder



Nano-size



- Micro-meter grains

- Nano-meter grains



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